FUEL OIL FOR USE BOTH IN INTERNAL COMBUSTION IN ENGINE AND FUEL CELL

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Abstract

A fuel oil for use both in an internal combustion engine and in a fuel cell containing 50 % by volume or more of an alkylate gasoline, and, optionally, 1 to 50 % by volume of isopentane, 1 to 12 % by volume of a hydrocarbon having 4 carbon atoms, 7 % by volume or less of an oxygen-containing compound, and 1 to 30 % by volume of a desulfurized light naphtha; and a fuel oil for use both in an internal combustion engine and in a fuel cell containing 10 to 60 % by volume of a desulfurized light naphtha, 40 to 90 % by volume of a benzene-free reformed gasoline and 0 to 10 % by volume of a hydrocarbon having 4 carbon atoms. Each of the above fuel oils is a fuel oil for a fuel cell which can produce hydrogen with good efficiency, has no adverse effect on reforming catalysts and electrodes for a fuel cell, and is reduced in deactivation of reforming catalysts and the like, and a fuel oil for an internal combustion engine which has a high octane number and can be used without causing knocking or the like.

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TITLE : FUEL OIL COMBINEDLY USEFUL FOR INTERNAL COMBUSTION ENGINE AND FUEL CELL

ABSTRACT : PROBLEM TO BE SOLVED: To obtain both a fuel oil for a fuel cell capable of efficiently producing hydrogen, not exerting a bad influence on a reforming catalyst and a fuel cell electrode, having a slight deterioration of a refoming catalyst, etc., and a fuel oil combinedly useful for an internal combustion engine and a fuel oil, having a high octane number, usable without causing a knocking, etc., when used as a fuel oil for an intemal combustion engine of an automobile.

SOLUTION: This fuel oil combinedly useful for an internal combustion engine and a fuel cell comprises ≥50 vol.% of an alkylate gasoline, and, if necessary, 1-50 vol.% of isopentane, 1-12 vol.% of a 4C hydrocarbon, ≤7 vol.% of an oxygen-containing containing compound and 1-30 vol.% desulfurized light naphtha. Alternatively, the fuel oil combinedly useful for an intemal combustion engine and a fuel cell comprises 10-60 vol.% of desulfurized light naphtha, 40-90 vol.% of a benzene-free reformed gasoline and 0-10 vol.% of a 4C hydrocarbon.

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Catalytic Autothermal Reforming of Hydrocarbon Fuels for Fuel Cell Systems

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Introduction

Fuel cell development has seen remarkable progress in the past decade because of an increasing need to improve energy efficiency as well as to address concerns about the environmental consequences of using fossil fuel for the propulsion of vehicles.[1] The lack of an infrastructure for producing and distributing H_2 has led to a research effort to develop on-board fuel processing technology for reforming hydrocarbon fuels to generate H_2.[2] The primary focus is on reforming gasoline, because a production and distribution infrastructure for gasoline already exists to supply internal combustion engines.[3] Existing reforming technology for the production of H_2 from hydrocarbon feedstocks used in large-scale manufacturing processes, such as ammonia synthesis, is cost prohibitive when scaled down to the size of the fuel processor required for transportation applications (50-80 kWe) nor is it designed to meet the varying power demands and frequent shutoffs and restarts that will be experienced during normal drive cycles. New reforming reactor technology will be required to meet the volume, weight, and cost targets, and operational characteristics required of a fuel processor for transportation applications. New reforming catalysts will be required that exhibit a higher activity and better thermal and mechanical stability than reforming catalysts currently used in the production of H_2 for large-scale manufacturing processes.

Hydrocarbon fuels can be reformed to produce H_2 by several reaction processes, including steam reforming, partial oxidation, and autothermal reforming. *Steam reforming* (Eq. 1) involves the reaction of steam with the fuel in the presence of a catalyst to produce H_2 and a mixture of CO and CO_2.

$$C_nH_mO_p + H_2O \Rightarrow H_2 + CO/CO_2,\ \Delta H^\circ_{298} >> 0 \qquad \text{(Eq. 1)}$$

Steam reforming is highly endothermic with the heat required for the reaction being quite significant to sustain acceptable reaction rates. The heat is generated by oxidizing part of the fuel external to the reformer where it is then transferred to the reformer via a heat exchanger. Reaction rates are generally limited by heat and mass transfer to the reactor and not by reaction kinetics. *Partial oxidation* (Eq. 2) involves the reaction of a substoichiometric amount of oxygen relative to complete combustion, usually supplied as air, to produce H_2, and a mixture of CO and CO_2.

$$C_nH_mO_p + O_2 \Rightarrow H_2 + CO/CO_2,\ \Delta H^\circ_{298} < 0 \qquad \text{(Eq. 2)}$$

The oxidation reaction is highly exothermic and reaction rates are generally very rapid. Unlike steam reforming, partial oxidation can be conducted with or without a catalyst. In the absence of a catalyst, the oxidation occurs in the gas phase and high temperatures (>1000°C) are required to achieve rapid reaction rates. Coking is a problem for gas phase oxidation. In the presence of a catalyst, rapid reaction rates can be achieved at considerably lower temperatures. *Autothermal reforming* (Eq. 3) involves the reaction of fuel, steam, and oxygen and utilizes the heat generated in the partial oxidation reactions to drive the endothermic steam reforming reactions.

$$C_nH_mO_p + O_2 + H_2O \Rightarrow H_2 + CO/CO_2,\ \Delta H^\circ_{298} < 0 \qquad \text{(Eq. 3)}$$

As written in Eq. 3, the reaction can be either endothermic or exothermic depending on the relative ratios of O_2:C and H_2O:C. For autothermal reforming the ratios are selected such that the reaction is slightly exothermic. As discussed for partial oxidation, the oxidation reactions can be conducted with or without a catalyst. The use of a catalyst for the oxidation reactions is preferred to allow for a lower reaction temperature.

The choice of the reaction process for on-board reforming depends on the operating characteristics (e.g., varying power demand, rapid startup, frequent shutdowns) for transportation applications. Steam reforming results in the highest yield of H_2 but has heat transfer limitations. Autothermal reforming and partial oxidation may be self-sustaining but result in lower H_2 yields due to the N_2 dilution because air and not pure oxygen is used. Because steam reforming is heat and mass transfer limited, it does not respond rapidly to changes in the power demand (i.e., "load following"), which would be frequently experienced during a normal driving cycle. When power demand rapidly decreases, the catalyst can overheat, causing sintering, which in turn results in a loss of activity. Autothermal reforming can overcome the load following limitations of steam reforming since the heat required for the endothermic reactions is generated within the catalyst bed, a property that allows for more rapid response to changing power demands and faster startup.[4] The lower operating temperature of catalytic autothermal reforming has several advantages including less complicated reactor design, wider choice of materials of construction, and lower fuel requirements during startup over the higher operating temperature of partial oxidation or the endothermic steam reforming for transportation applications.[5]

At Argonne National Laboratory, we are developing new catalysts for autothermal reforming.[6] Our catalysts are derived from solid oxide fuel cell materials, where a transition metal is supported on an oxide-ion-conducting substrate, such as ceria, zirconia, or lanthanum gallate that has been doped with a small amount of a non-reducible element, such as gadolinium, samarium, or zirconium. Ceria-based materials are being investigated as potential catalysts for CO and hydrocarbon oxidation reactions because of the redox and oxygen storage/release properties of ceria.[7] The catalytic activity of ceria can be further enhanced by the addition of dopants, such as Gd^{3+} or Sm^{3+}, which have been shown to increase the number of oxygen vacancies, improve the oxygen mobility and oxygen ion conductivity, and enhance the redox and oxygen storage/release properties of ceria. The role of defect chemistry and the surface oxygen vacancies in determining the catalytic behavior of these metal/mixed oxide systems is well known.[8]

Experimental

A mixed metal oxide substrate consisting of CeO_2 and Gd_2O_3 (referred to as CGO) at a ratio of 4:1 Ce:Gd was synthesized by either a glycine-nitrate process or coprecipitation of metal salt precursors followed by calcination at 600-1000°C. A Group VIII transition metal selected from the noble metals (Pt, Ru, or Rh) or non-noble metals (Co or Ni) was loaded onto the CGO substrate using the incipient wetness technique. Metal loadings ranged from 0.1 to 1 wt%.

These materials were tested for autothermal reforming of isooctane (2,2,4-trimethylpentane), which is used as a single component surrogate for gasoline. These tests were conducted using ~1-2 g of material in a microreactor system equipped with an on-line gas chromatograph. Thermocouples were located at the top and the bottom of the catalyst bed. The temperature at the bottom of the catalyst is reported for these experiments.

These materials were also tested for autothermal reforming of isobutane using a temperature-programmed reaction procedure. In this procedure, ~50 mg of material was contacted with a gas mixture consisting of 0.2 mL/min of isobutane, 0.4 mL/min O_2, 0.8 mL/min H_2O, and 48.6 mL/min He. The catalyst was heated from 100 to 800°C at a rate of 2°C/min. The reaction products were determined by mass spectroscopy. These experiments were conduct using a Zeton Altamira AMI-100 Chemisorption Unit.

Results and Discussion

For autothermal reforming of isooctane with a feed ratio O_2:C=0.5 for oxygen and H_2O:C=1.1 for water, a maximum yield of 12.2 moles of H_2 per mole of isooctane in the feed is predicted at a temperature of ~700°C based on thermodynamic equilibrium. Figure 1 shows the H_2 yield produced from autothermal reforming of isooctane over the temperature range of 500-800°C in the presence of the various transition metals supported on CGO. Near equilibrium yields of H_2 are observed for all five metals supported on CGO at ~700°. The H_2 yields for three noble metals (Pt-11.4 moles of H_2 per mole of isooctane in the feed, Ru-11.4 moles of H_2 per mole of isooctane in the feed, Rh-10.9 moles of H_2 per mole of isooctane in the feed) were slightly higher than the H_2 yield for the non-noble metals (Ni - 10.3 moles of H_2 per mole of isooctane in the feed and Co - 10.3 moles of H_2 per mole of isooctane in the feed). Although the H_2 yields for the non-noble metals were slightly less than the H_2 yields for the noble metals, there is considerable interest in a non-noble metal catalyst from a cost viewpoint. For all metals, the conversion of isooctane was >99% at temperatures above 700°C. At temperatures below 600°C, the H_2 yields for Ru, Rh, and Ni were significantly higher than the H_2 yields for Pt or Co. Generally, Rh, Ru, and Ni are considered to be more active than Pt or Co for steam reforming.[5]

The yield of the primary reaction products (H_2, CO, CO_2, and CH_4) produced from the autothermal reforming of isooctane catalyzed by Rh-CGO over the temperature range of 500-700°C is shown in Figure 2. The yields of H_2 and CO, which are produced by steam reforming or possibly CO_2 reforming ($CO_2 + CH_4 \Leftrightarrow 2H_2 + 2CO$), increase as the temperature increases. The CO_2 yield decreases as the temperature increases due to either the water-gas shift reaction ($H_2O + CO \Leftrightarrow H_2 + CO_2$), which favors the reactants (H_2O + CO) as the temperature increases, or possibly CO_2 reforming. The CH_4 yield is observed to go through a maximum at ~600°C. CH_4 can be produced by at least two possible pathways, thermal cracking of isooctane or CO hydrogenation ($CO + 3H_2 \Rightarrow CH_4 + H_2O$). Once formed, CH_4 can be reformed to generate additional H_2. CH_4 is considered to be more difficult to reform than higher carbon number alkanes, which can explain why a maximum in the CH_4 yield is observed. Similar trends in the primary product distribution as a function of temperature were observed for the other metals supported on CGO although the temperature at which the maximum CH_4 yield was observed varied among the various metals.

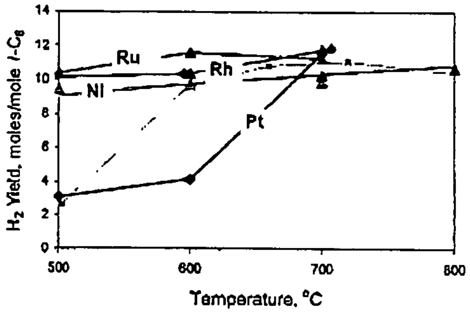

Figure 1. H_2 yield (moles of H_2/mole of i-C_8 in the feed) as a function of temperature for autothermal reforming of isooctane (O_2:C=0.5, H_2O:C=1.1) catalyzed by various transition metals supported on CGO. The gas-hourly space velocities ranged from 5,000-19,000 h^{-1}.

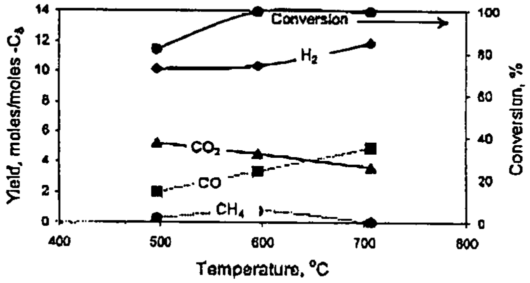

Figure 2. The primary product yield as a function of temperature for autothermal reforming of isooctane (O_2:C=0.5, H_2O:C=1.1) catalyzed by Rh-CGO. The gas-hourly space velocity was 19,000 h^{-1}.

Temperature-programmed reaction studies of isobutane autothermal reforming catalyzed by Rh-CGO (Figure 3) or Pt-CGO (Figure 4) show differences in the activity of the two metals for catalyzing the oxidation and reforming reactions. For Pt-CGO, all of the O_2 is consumed at temperatures below 200°C, whereas for Rh-CGO, the consumption of O_2 begins at a higher temperatures, >300°C. For Pt-CGO and Rh-CGO, only deep oxidation products, H_2O and CO_2, are observed when O_2 is present in the product gas. No H_2 or CO is observed when O_2 is present in the product gas. Even if H_2 and CO are produced, they are rapidly oxidized to H_2O and CO_2 respectively. The difference in the activity of the two metals may be due to the fact that Pt is more easily reduced than Rh under autothermal reforming conditions. XPS analysis of Pt-CGO catalysts after autothermal reforming indicates that both oxidized and metallic Pt is present. Only after all of the O_2 is consumed, are H_2 and CO, which are products of steam reforming or possible CO_2 reforming, observed in the product gas. For Rh-CGO, a near maximum yield of H_2 is observed when light-off occurs at ~380°C. For Pt-CGO, the maximum yield of H_2 is not observed until ~650°C. In summary, Pt-CGO is more active for oxidation and Rh-CGO is more active for steam reforming based on a comparison of the temperatures at which the two reactions occurred for each catalyst.

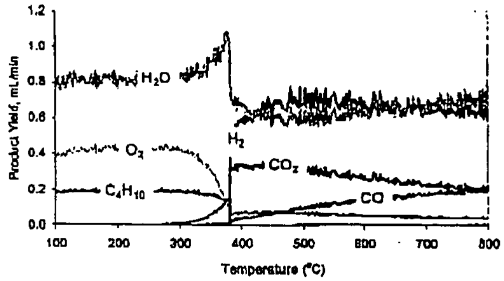

Figure 3. Primary product yield for autothermal reforming of isobutane (O_2:C=0.5, H_2O:C=1.0) catalyzed by Rh-CGO using temperature-programmed reaction. The temperature ramp rate is 2°C/min.

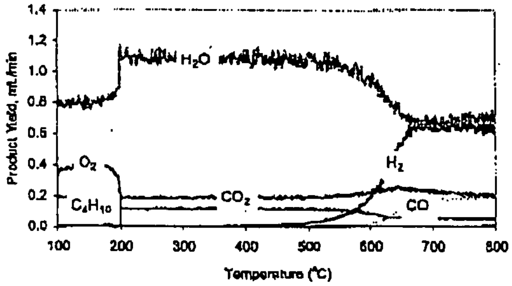

Figure 4. Primary product yield for autothermal reforming of isobutane (O_2:C=0.5, H_2O:C=1.0) catalyzed by Pt-CGO using temperature-programmed reaction. The temperature ramp rate is 2°C/min.

Conclusions

Catalysts consisting of a Group VIII transition metal, (Ni, Co, Rh, Ru, or Pt) supported on CGO were shown to produce near equilibrium yields of H_2 at ~700°C for the autothermal reforming of isooctane under the reaction conditions investigated. Temperature-programmed reaction studies of the autothermal reforming of isobutane catalyzed by these materials showed that the metals exhibited different activities for the oxidation and steam reforming reactions. Oxidation reactions were observed to occur at a lower temperature on Pt-CGO compared to Rh-CGO; however, steam reforming reactions were observed to occur at lower temperature on Rh-CGO compared to Pt-CGO.

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